n^{20}_D 1.5449 and d^{20}_4 0.8083, when pyrolyzed under optimum conditions (a temperature of 400° and a through-put of 250 g. per hour) gave a product of n^{20}_D 1.4790. Considerable variations in through-put rate or pyrolysis temperature may be made without materially altering the extent of isomerization (as judged by change in refractive index).

A portion of the pyrolyzate obtained in this way (n^{20}_D 1.4795; d^{20}_4 0.8358) when fractionally distilled *in vacuo* was found to contain about 30% of α-pyronene and about 45% of β-pyronene, together with some unchanged *allo*-ocimene, dimer, and other unidentified hydrocarbons. The fractions containing the highest concentrations of α- and β-pyronene had the following characteristics: α-pyronene, b. p. 54–56° at 20 mm., d^{20}_4 0.8272, n^{20}_D 1.4672; β-pyronene, b. p. 62–64° at 20 mm., d^{20}_4 0.8481, n^{20}_D 1.4800. From these fractions the characteristic maleic anhydride adducts of the respective pyronenes could be obtained in excellent yield.

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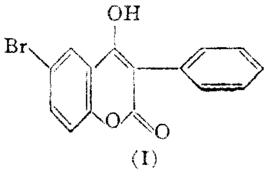
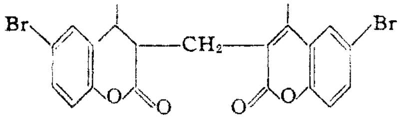
Brominated 4-Hydroxycoumarins

BY CHARLES F. HUEBNER AND KARL PAUL LINK

The synthesis of bromine-containing anticoagulants related to the original anticoagulant 3,3′-methylenebis-(4-hydroxycoumarin),[1] is described in this note. 3-Phenyl-4-hydroxy-6-bromocoumarin (I) was prepared by an intramolecular Claisen condensation[2] of methyl 2-phenylacetoxy-5-bromobenzoate. By the same type reaction, 4-hydroxy-6-bromocoumarin was prepared and by reaction with formaldehyde was converted to 3,3′-methylenebis-(4-hydroxy-6-bromocoumarin) (II).



(I)



(II)

Experimental

Methyl 2-Phenylacetoxy-5-bromobenzoate.—A mixture of 60 g. of phenylacetyl chloride and 90 g. of methyl 5-bromosalicylate[3] was heated under reflux on a steam-bath for four hours. Pyridine (30 ml.) was added and the heating was continued for four hours longer. The resulting oil was dissolved in ether and extracted successively with water, hydrochloric acid solution, and sodium carbonate solution. The ether solution was dried and the ester was crystallized by the addition of petroleum ether. After two recrystallizations from ethanol the product weighed 56 g., m. p. 68–70°. *Anal.* Calcd. for $C_{15}H_{10}O_3Br(OCH_3)$: OCH_3, 8.9. Found: OCH_3, 8.8.

3-Phenyl-4-hydroxy-6-bromocoumarin (I).—To a well-stirred melt of 20 g. of methyl 2-phenylacetoxy-5-bromobenzoate contained in a round bottom flask, 1.3 g. of sodium was added and the temperature was raised to 200°, at which point a spontaneous reaction occurred. External heating was discontinued and after thirty minutes the glassy mass was cooled and dissolved in water. The aqueous solution was acidified to *p*H 6, extracted with ether, and further acidified to *p*H 5. The product crystallizing between these two *p*H's was filtered and recrystallized twice from acetic acid. The yield was 8 g., m. p. 252–254°. *Anal.* Calcd. for $C_{15}H_9O_3Br$: C, 56.8; H, 2.8. Found: C, 57.0; H, 2.9.

Methyl 2-Acetoxy-5-bromobenzoate.—To 30 g. of methyl 5-bromosalicylate was added 80 ml. of acetic anhydride and 1 ml. of sulfuric acid. After thirty minutes the mixture was poured into ice water, the oil was washed with sodium carbonate solution, and crystallized from methanol–water. The yield was 20 g., m. p. 33–35°. *Anal.* Calcd. for $C_9H_6O_3Br(OCH_3)$: OCH_3, 11.4. Found: OCH_3, 11.3.

3,3′-Methylene bis-(4-hydroxy-6-bromocoumarin) (II)—4-Hydroxy-6-bromocoumarin was prepared in a manner similar to that described for 3-phenyl-4-hydroxy-6-bromocoumarin except that the reaction was run in kerosene and the final product was collected between *p*H 5.6 and 2.5. From 176 g. of ester, and 14.8 g. of sodium in 300 ml. of kerosene, 92 g. of crude 4-hydroxy-6-bromocoumarin was obtained. This crude product was refluxed in ethanol with an excess of formaldehyde. The methylenebis product which was extremely insoluble in alcohol crystallized after one hour. This product was filtered and recrystallized from cyclohexanone, yield 40 g., m. p. 326–327°. *Anal.* Calcd. for $C_{19}H_{10}O_6Br_2$: C, 46.2; H, 2.0. Found: C, 46.3; H, 2.3.

3,3′-Methylene bis-(4-hydroxy-6-bromocoumarin) dimethyl ether was prepared by the diazomethane technique. The ether was recrystallized from β-dichloroethyl ether, m. p. 218–220°. *Anal.* Calcd. for $C_{19}H_8O_4Br_2(OCH_3)_2$: OCH_3, 11.8. Found: OCH_3, 12.0.

DEPARTMENT OF BIOCHEMISTRY
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(1) Stahmann, Huebner and Link, *J. Biol. Chem.*, **138**, 513 (1941).

(2) Stahmann, Wolff and Link, THIS JOURNAL, **65**, 2285 (1943).

(3) Peratoner, *Gazz. chim. ital.*, **16**, 405 (1886).

The Dielectric Constants and Dipole Moments of Acetylenic Ethers

BY THOMAS L. JACOBS, JOHN D. ROBERTS AND W. G. MACMILLAN

The dielectric constants of pure samples of ethoxy-, butoxy- and phenoxy-acetylene[1] were measured at 25° by the heterodyne beat method as described by Wood and Dickinson.[2]

The frequency of the standard circuit was adjusted to that of the carrier wave of radio station KFAC which broadcasts on a frequency of 1300 kilocycles,[3] and the increment of capacity was

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(1) The acetylenic ethers were carefully refractionated samples prepared in connection with other investigations: Jacobs, Cramer and Hanson, THIS JOURNAL, **64**, 223 (1942); Jacobs, Cramer and Weiss, *ibid.*, **62**, 1849 (1940). The phenoxyacetylene was prepared by Dr. Wm. Penn Tuttle, Jr.

(2) Wood and Dickinson, *ibid.*, **61**, 3259 (1939).

(3) Otto and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **6**, 187 (1934).